Water Under the Extreme Conditions of Planetary Interiors

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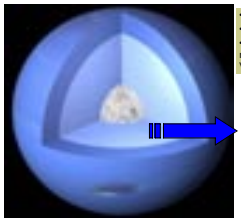
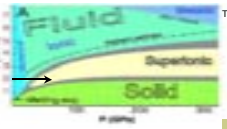
Water inside giant planets may have exotic properties



•Uranus, Neptune: 56% H_2O, •36% CH_4, 8% NH_3
✓hot ice" mixture contributes to magnetic field measurements by Voyager 2 spacecraft

Simulations of water under conditions within large planets show the existence of a superionic phase

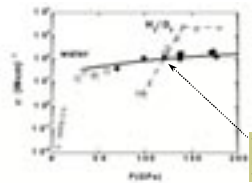


The superioninc phase is defined as follows:
1. Oxygen atoms form lattice
2. Rapid proton dissociation via hopping between lattice points
3. Protons need oxygen lattice to hop between sites

Cavazzoni et al., Science, **283**, 44, 1999.

High conductivity within planetary core is predicted to be the source of magnetic fields measured by satellite

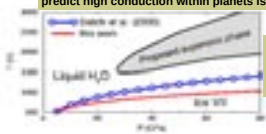
Studies of "synthetic" planetary interiors show H^+ conductivity occurs deep within Uranus and Neptune



•Experimental results show high pressure yields high ionic conductivity
•Due to $H_2O \rightarrow 2H^+ + O^{2-}$

Chau et al., JCP, **114**, 1361 (2001)

Later results do not observe superionic phase and predict high conduction within planets is due to H_3O^+



Recent experimental results show no evidence of oxygen atom lattice, implying no superionic phase

Frank et al., PRL, submitted

•*Ab initio* MD simulations confirm lack of O lattice
•Predict shortlived H_3O^+ as major ionic conductor

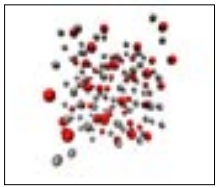
Schwegler et al., PRL, **87**, 265501-1, 2001.

LLNL supercomputers allow us to solve the controversy

- We simulated 54 H2O molecules along the *2000K isotherm*, from densities of 1.57—3.00 g/cc, in order to determine the following:

1. Structure of water at high temperature, high pressure
   - Radial distribution functions
   - Is there an oxygen lattice?
2. Dynamics
   - Investigate vibrational structure
   - Compare oxygen and hydrogen diffusion
3. Ionic species and lifetimes

What residence time constitutes a molecule?



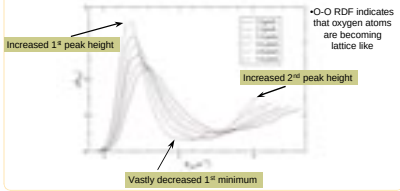
Simulation at 2.40 g/cc, 2000K

- The MCR supercomputer allows us to run simulations for much longer times than previously possible.
- We can apply chemical Transition State Theory to re-analyze the results

CPMD *ab initio* molecular dynamics software
- Version 3.82
- BLYP gradient corrected exchange correlation energy functional
- Troullier-Martins pseudopotential

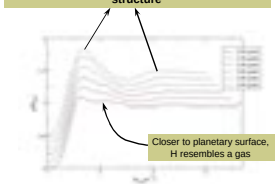
Structural properties reveal glassy nature of "extreme" water

O-O Radial Distribution Function indicates a glassy phase by 2.60 g/cc



•O-O RDF indicates that oxygen atoms are becoming lattice like

Deeper within a giant planet, we see hydrogen structure

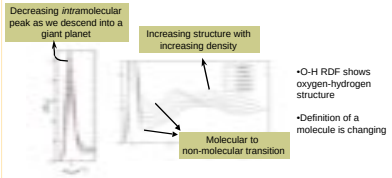


Closer to planetary surface, H resembles a gas

Superionic structure occurs deeper within planet than previously thought

Dynamic properties show completely novel aspect of chemical bonding

Protons are "jumping" between lattice points



Decreasing *intra*molecular peak as we descend into a giant planet

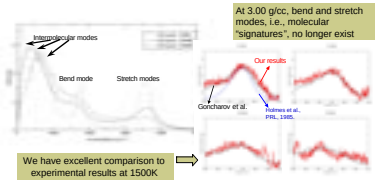
Increasing structure with increasing density

•O-H RDF shows oxygen-hydrogen structure

•Definition of a molecule is changing

Molecular to non-molecular transition

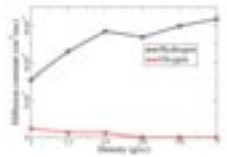
Vibrational spectra at high density do not show presence of typical molecules



At 3.00 g/cc, bend and stretch modes, i.e., molecular "signatures", no longer exist

We have excellent comparison to experimental results at 1500K.

Protons exhibit superionic diffusion in absence of oxygen lattice

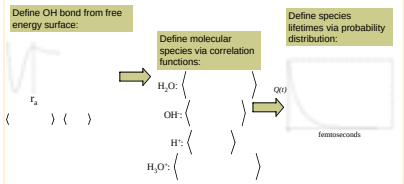


Hydrogens consistently diffuse much faster than oxygens

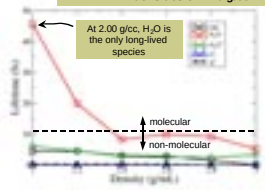
Rapid conduction may occur inside planets even in absence of oxygen lattice

Ionic species and lifetimes are analyzed via ideas from Transition State Theory

We have developed a "language" for describing interesting dissociation kinetics



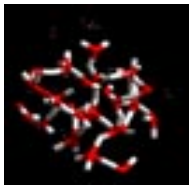
Average species lifetimes are fleetingly small at densities of 2.40 g/cc



At 2.00 g/cc, H_2O is the only long-lived species

By 2.40 g/cc, all species present in the simulation are too short lived to be defined as molecular

The majority of species in the water are short lived O—H bond networks



•Snapshot from 3.0 g/cc, 2000 K

At lower densities, H_2O is the predominant species, but still evidence of chains

O—H bonding at these conditions is ca. 80% covalent!

O—H network could play role in planetary dynamo mechanism

Summary

We now have an accurate description of water in Giant Planet interiors:

Pt. 1: Oxygen atoms and hydrogens are disordered
- Superionic diffusion does occur

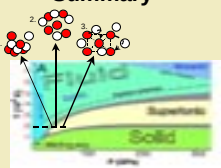
Pt. 2: Oxygens have slowed down and exhibit some order
- Protons still have rapid diffusion

Pt. 3: Oxygen atoms have strong order
- Protons conduct via hopping mechanism

Both sides of controversy are correct

Superionic phase of water is the likely source of the large magnetic fields of Uranus and Neptune.

O—H bond network appears to be a new state of matter!



Definitive experiments are currently being conducting in the XChem group at LLNL

Future Work:

Simulations of "synthetic" Uranus on new Thunder supercomputer:

•Construct configuration of several hundred atoms and simulate for several picoseconds
•Requires millions of CPU hours – **can only be accomplished at LLNL**
•We will investigate the formation of amino acids and proteins

LLNL's Thunder will let us investigate the inception of life on other planets

Publications:

N. Goldman, R.S. Fellers, M.G. Brown, L.B. Braly, C.J. Keoshian, C. Leforestier, R.J. Saykally, "Spectroscopic determination of the water dimer intermolecular potential energy surface," *J. Chem. Phys.*, **116** (23), 2002, 10148-10163.

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